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THE OZONE OXIDATION OF ETHYLENE AS IT PERTAINS TO AIR POLLUTION*

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ABSTRACT

The ozone oxidations of hydrocarbons are important reactions in air pollution because they represent a significant step in the formation of photochemical smog. The formation of smog is a non-equilibrium process, dependent on the rates of a sequence of reactions involving nitrogen oxides, atomic oxygen, ozone, and hydrocarbons. This paper contains (1) a review of published data on the kinetic rate constants for the ozone oxidation of hydrocarbons, and (2) the results of an experimental study of ozone decomposition and ozone-ethylene reaction stoichiometry. The review includes published data on alkanes, alkenes, alkynes, aromatics, and oxygenated hydrocarbons.

The experimental study was made using cylinder ozone dissolved in Freon-13, and involved monitoring the pressure changes that occurred during reaction in a constant volume glass reactor. With this technique, the ozone decomposition rate was much higher than that predicted by published data, apparently from catalytic effects or reactions involving the Freon-13. In the ozone oxidation of ethylene the effect of the initial reactant ratio was significant, and the data indicated that competing reactions were involved. Finally, several factors requiring clarification are cited, and suggestions for additional experimental work are included.

INTRODUCTION

There is evidence that more than eighty gaseous and more than ninety suspended particulate organic compounds are present in contaminated urban atmospheres (Stern, 1962). This is probably a conservative estimate when one considers the possible sources of organic emissions such as automobiles and trucks, petroleum refining and storage, organic solvent usage, fuel combustion, and incineration (Chass et al., 1960). As an example, the daily hydrocarbon emissions in Los Angeles County alone are estimated to be more than 2000 tons (Air Conservation, 1965). Altshuller (1966), Neligan (1962), Stephens and Burleson (1967), and Williams (1965) have identified and tabulated specific organic compounds found in the atmosphere. The lists include alkane, alkene, alkyne, aromatic, and oxygenated hydrocarbons. The lower molecular weight alkanes and alkenes appear to be present in the highest concentrations.

Photochemical smog has received considerable attention, and the generally accepted overall reaction scheme involves the following steps:

$$NO_2 + h\nu \rightarrow NO + O \quad (1)$$

$$O + O_2 \rightarrow O_3 \quad (2)$$

$$O_3 + \text{Hydrocarbons} \rightarrow \text{Products} \quad (3)$$

$$O + \text{Hydrocarbons} \rightarrow \text{Products} \quad (4)$$

where $h\nu$ represents the energy of the incident radiation. The photodissociation of NO_2 forms atomic oxygen which can react directly with the hydrocarbon pollutants to form part of the smog or with moelcular oxygen to form ozone. The ozone, in turn, can also react with the hydrocarbons. As a group, the alkenes appear to be the most reactive and efficient at producing smog. The suggested detailed mechanism involves free radical formation (Stern, 1968, p. 177-178), and the potential number of pollutants resulting from interaction of the reaction intermediates and products is thereby greatly increased. The ozone that is produced naturally in the atmosphere appears to be of minor importance in the overall process.

One of the main supports for the photochemical mechanism is that a mixture of nitrogen oxides and hydrocarbons in combination with ultraviolet light energy can produce, in the laboratory, effects which are identical or

very similar to those associated with the photochemical smog around Los Angeles. Altshuller and Bufalini (1965) have presented an excellent review on the photochemical aspects of air pollution, including observations on effects as well as mechanistic considerations. Eye irritation (Altshuller, 1965; Buchberg, 1963; Schuck, 1960) and plant damage (Altshuller, 1965; Middleton, 1961), indicative of the conditions actually found, have been duplicated in laboratory experiments.

In these laboratory experiments the major products observed in the irradiated hydrocarbon - nitric oxide mixtures included oxidant (demonstrated to be primarily ozone), aldehydes and ketones, carbon monoxide, and organic nitrates. The organic nitrates are normally accounted for by reactions such as

$$RCO\cdot + NO_2 + O_2 \rightarrow RCO_3NO_2 \qquad (5)$$

Lesser amounts of epoxides, alcohols, esters, and peroxides have been reported (Altshuller and Bufalini, 1965).

Since the reactant concentrations are low, the rate constant for a given reaction must be relatively large if the reaction is to play a significant role in smog formation. It appears that practically all of the organic oxidation reactions are at least initiated thru attack by either atomic oxygen or ozone. In the irradiation of nitrogen oxide - hydrocarbon mixtures, however, it has been found that the rate of disappearance of the hydrocarbon cannot be explained by considering only the reactions of the hydrocarbon with ozone and atomic oxygen. Stephens (1966) cited some of the

work upon which this conclusion was based. Bufalini and Altshuller (1967) termed this difference an excess rate. In some cases, even under the most favorable conditions, less than half of the rate of disappearance of hydrocarbon could be explained by the reactions with atomic oxygen and ozone. Bufalini and Altshuller (1967) have suggested and presented some evidence that free radical attack of the olefin (started by the atomic oxygen - hydrocarbon reaction) may, at least in part, be responsible for these apparent synergistic effects. However, to the best of our knowledge the effect of irradiation on the rates of the ozone-hydrocarbon and atomic oxygen-hydrocarbon reactions has not been studied.

In this paper the published data on the kinetic rate constants for ozone-hydrocarbon reactions (Reaction 3) are reviewed for alkane, alkene, alkyne, aromatic, and oxygenated hydrocarbons. Also, results of some preliminary investigation on the ozone-ethylene reaction in particular are presented. Factors that need clarified are cited and suggestions are included for additional work. Data on the kinetics of the atomic oxygen-hydrocarbon reactions (Reaction 4) have been presented by Ford and Endow (1957), Elias and Schiff (1960), Elias (1963), Altshuller and Bufalini (1965), and Stephens (1966).

REVIEW OF OZONE - HYDROCARBON KINETICS

Ozone - Alkane Hydrocarbon Reactions

The available experimental data indicate that the alkanes exhibit a slower rate of reaction with ozone than either the alkenes, alkynes, or aromatics. Table I lists published data on the kinetic constants of the ozone - alkane hydrocarbon reactions. The reaction rate constants are based on the assumption of a second order reaction, first order with respect to each reactant. In the studies the initial concentration of both reactants was far in excess of those found in the lower atmosphere of urban centers. Assuming normal atmospheric pressure and 25°C, these initial reactant concentrations ranged from about 40,000 to 700,000 ppm by volume. Where several measurements exist, the data agree quite closely.

Ozone - Alkene Hydrocarbon Reactions

The alkene hydrocarbons have received the most attention relative to reaction with ozone. Tables II, III, and IV contain the published reaction rate constant data for the ozone-alkene systems.

As a group, the alkenes show the fastest rate of reaction with ozone. This is due to the high susceptibility of the carbon - carbon double bond to oxidative attack.

TABLE I

SUMMARY OF PAST WORK ON OZONE - ALKANE REACTION KINETIC CONSTANTS -

Compound	Oxygen Present	Initial Ozone Concentration (Moles/Liter)	Initial Hydrocarbon Concentration (Moles/Liter)	Pre-Exponential Factor[a] (Liters/Mole Sec.)	Activation Energy[a] (kcal/Mole)	k at 25°C[b] (Liters/Mole Sec.)	Reference
Methane	Yes	1.5×10^{-2}	2.9×10^{-2}	1.63×10^{8}	15.35	0.82×10^{-3}	Dillemuth (1962
Methane	Yes	(c)	(c)	7.2×10^{7}	14.9	0.85×10^{-3}	Schubert (1956
Methane	No	1.5×10^{-2}	2.9×10^{-2}	1.43×10^{7}	13.9	0.84×10^{-3}	Dillemuth (1962
Ethane	Yes	$< 1.8 \times 10^{-3}$	1.8×10^{-2}	1.24×10^{8}	13.9	7.40×10^{-3}	Morrissey (1963
Ethane	No	$< 1.8 \times 10^{-3}$	1.8×10^{-2}	3.50×10^{8}	14.7	5.79×10^{-3}	Morrissey (1963
Propane	Yes	---	1.8×10^{-2}	3.1×10^{6}	12.1	4.1×10^{-3}	Schubert (1956
Propane	Yes	$< 1.6 \times 10^{-3}$	1.8×10^{-2}	2.12×10^{8}	14.3	4.34×10^{-3}	Morrissey (1963
Propane	No	$< 1.6 \times 10^{-3}$	1.8×10^{-2}	1.17×10^{8}	14.6	3.75×10^{-3}	Morrissey (1963
n-Butane	Yes	(c)	(c)	8.2×10^{5}	11.1	5.9×10^{-3}	Schubert (1956
Isobutane	Yes	(c)	(c)	4.4×10^{8}	10.3	12.2×10^{-3}	Schubert (1956

Notes: (a) Activation energy, E, defined by: $k = Ae^{-E/RT}$, where A is pre-exponential factor.

(b) Assumed rate equation: $-\frac{dC_{HC}}{dt} = k\, C_{O_3}\, C_{HC}$

(c) No mention of initial reactant concentrations; inspection of data indicated concentrations were in same range as reported for the other studies.

The mechanism of attack of this double bond by ozone has received substantial attention, and Bailey (1958) has presented a detailed review. The generally accepted mechanism is attributed to Criegee (1959). The ozone attacks the double bond producing a zwitterion and an aldehyde.

$$R_1HC = CHR_2 + O_3 \rightarrow R_1HC^+-O-O^- + O = CHR_2 \qquad (6)$$

In the liquid phase, these may recombine to form the ozonide,

$$R_1HC^+-O-O^- + O = CHR_2 \rightarrow R_1CH\begin{matrix}O-O\\ \diagdown\quad\diagup\\ O\end{matrix}CHR_2 \qquad (7)$$

or the zwitterion may undergo a variety of other reactions depending on what reactive species are present. In the gas phase at temperatures normally found in the lower atmosphere, it is doubtful if the ozonide structure exists.

The rate constants shown in Table II are all based on second order kinetics - first order with respect to both the ozone and the olefin. Substantial data were found in the literature with good agreement for many of the compounds. However, others such as cis-2-butene, 2-methyl-2-butene, and trans-2-butene had rate constants that differed by a factor of twenty to fifty.

Many of the data in Table II for the reactions between alkenes and ozone were obtained by Vrbaski and Cvetanovic (1960). They used a method of competing reactions and determined only relative rate constants. This method was based on the relative amounts of each product formed when two

TABLE II

SUMMARY OF PAST WORK ON OZONE - ALKENE REACTION KINETIC CONSTANTS

Compound	Oxygen Present	Initial Ozone Concentration (Moles/Liter)	Initial Hydrocarbon Concentration (Moles/Liter)	Pre-Exponential Factor[a] (Liters/Mole Sec.)	Activation Energy[a] (kcal/Mole)	$k \times 10^{-3}$ at 25°C[b] (Liters/Mole Sec.)	Reference
Ethylene	Yes	10^{-5}	10^{-5}	(c)	(c)	1.8	Cadle (1952)
Ethylene	---	---	---	---	---	0.8	Hanst (1958)
Ethylene	Yes	10^{-4}	10^{-3}	---	---	1.4[f]	Vrbaski (1960)
Ethylene	Yes	10^{-7}	10^{-7}	1.7×10^{6}	4.2	1.6[g]	Bufalini (1965)
Propylene	Yes	10^{-8}	10^{-7}	---	---	3.8[e]	Cadle (1952)
Propylene	---	---	---	---	---	4.9	Hanst (1958)
Propylene	Yes	10^{-4}	10^{-3}	---	---	3.9[f]	Vrbaski (1960)
2-Methylpropene	---	---	---	---	---	3.7	Hanst (1958)
2-Methylpropene	Yes	10^{-4}	10^{-3}	---	---	2.8[f]	Vrbaski (1960)
2-Methylpropene	Yes	10^{-7}	10^{-7}	1.4×10^{6}	2.8	14.[g]	Bufalini (1965)
2-Methylpropene	Yes	10^{-7}	10^{-7}	---	---	8.8	Schuck (1960)
1-Butene	Yes	10^{-4}	10^{-3}	---	---	3.0[f]	Vrbaski (1960)
1-Butene	Yes	10^{-7}	10^{-7}	---	---	6.2[g]	Bufalini (1965)
2-Methyl-1-Butene	Yes	10^{-4}	10^{-3}	---	---	3.1[f]	Vrbaski (1960)
3-Methyl-1-Butene	Yes	10^{-4}	10^{-3}	---	---	2.3[f]	Vrbaski (1960)
2-Methyl-2-Butene	Yes	10^{-4}	10^{-3}	---	---	9.0[f]	Vrbaski (1960)
2-Methyl-2-Butene	Yes	10^{-7}	10^{-7}	---	---	450.[g]	Bufalini (1965)
2,3-Dimethyl-2-Butene	Yes	10^{-4}	10^{-3}	---	---	11.[f]	Vrbaski (1960)
Cis-2-Butene	Yes	10^{-7}	10^{-7}	---	---	200.[g]	Bufalini (1965)

TABLE II (Continued)

SUMMARY OF PAST WORK ON OZONE - ALKENE REACTION KINETIC CONSTANTS

Compound	Oxygen Present	Initial Ozone Concentration (Moles/Liter)	Initial Hydrocarbon Concentration (Moles/Liter)	Pre-Exponential Factor[a] (Liters/Mole Sec.)	Activation Energy[a] (kcal/Mole)	$k \times 10^{-3}$ at 25°C[b] (Liters/Mole Sec.)	Reference
Cis-2-Butene	---	---	---	---	---	29.	Hanst (1958)
Cis-2-Butene	Yes	10^{-4}	10^{-3}	---	---	10.(f)	Vrbaski (1960)
Trans-2-Butene	Yes	10^{-4}	10^{-3}	---	---	13.(f)	Vrbaski (1960)
Trans-2-Butene	Yes	10^{-7}	10^{-7}	3.6×10^{5}	0.2	260.(g)	Bufalini (1965)
1-1-Pentene	Yes	10^{-8}	10^{-7}	---	---	3.2(e)	Cadle (1952)
1-1-Pentene	---	---	---	---	---	4.5	Hanst (1958)
1-1-Pentene	Yes	10^{-4}	10^{-3}	---	---	2.9(f)	Vrbaski (1960)
Cis-2-Pentene	---	---	---	---	---	98.	Hanst (1958)
Cis-2-Pentene	Yes	10^{-4}	10^{-3}	---	---	7.8(f)	Vrbaski (1960)
Trans-2-Pentene	Yes	10^{-4}	10^{-3}	---	---	9.7(f)	Vrbaski (1960)
1-1-Hexene	Yes	10^{-7}	10^{-7}	(d)	(d)	6.1	Cadle (1952)
1-1-Hexene	---	---	---	---	---	6.1	Hanst (1958)
1-1-Hexene	Yes	10^{-6}	10^{-6}	---	---	5.5	Saltzmann (1959)
1-1-Hexene	Yes	10^{-4}	10^{-3}	---	---	3.5(f)	Vrbaski (1960)
1-1-Hexene	Yes	10^{-7}	10^{-7}	---	---	6.8(g)	Bufalini (1965)
1-1-Hexene	Yes	10^{-7}	10^{-7}	---	---	6.9	Schuck (1960)
-Heptene	Yes	10^{-8}	10^{-7}	---	---	4.9(e)	Cadle (1952)
3-Heptene (Cis + Trans)	---	---	---	---	---	53.	Hanst (1958)

TABLE II (Continued)

SUMMARY OF PAST WORK ON OZONE - ALKENE REACTION KINETIC CONSTANTS

Compound	Oxygen Present	Initial Ozone Concentration (Moles/Liter)	Initial Hydrocarbon Concentration (Moles/Liter)	Pre-Exponential Factor(a) (Liters/Mole Sec.)	Activation Energy(a) (kcal/Mole)	$k \times 10^{-3}$ at 25°C(b) (Liters/Mole Sec.)	Reference
1-Octene	Yes	10^{-8}	10^{-7}	---	---	4.9(e)	Cadle (1952)
1-Decene	Yes	10^{-8}	10^{-7}	---	---	6.6(e)	Cadle (1952)
Cyclohexene	Yes	10^{-8}	10^{-7}	---	---	35.(e)	Cadle (1952)
Cyclohexene	Yes	10^{-4}	10^{-3}	---	---	10.(f)	Vrbaski (1960)
1,3-Butadiene	---	---	---	---	---	4.9	Hanst (1958)
1,3-Butadiene	Yes	10^{-4}	10^{-3}	---	---	3.2(f)	Vrbaski (1960)

Notes: (a) Activation energy, E, defined by: $k = Ae^{-E/RT}$, where A is pre-exponential factor.

(b) Assumed rate equation: $-\frac{dC_{HC}}{dt} = k\, C_{O_3}\, C_{HC}$

(c) Found reaction independent of temperature between 30°C and 50°C.

(d) Found reaction independent of temperature between 8°C and 27°C.

(e) Assumed measured at 25°C.

(f) Investigators used method of competing reactions. Figures shown are relative reaction rate constants k_1/k_{ref} (relative to ethylene) multiplied by 1.4×10^3 (average of the three absolute rate constants).

(f) Measured at 30°C.

alkenes were mixed and allowed to react with ozone. It presupposed that no interactions occurred when the two olefins competed for ozone and that each product being monitored was formed only from the primary reaction with ozone. In their method, Reactions (8) and (9) were considered to be second order with the initial concentrations of the two competing olefins, A_1 and A_2, sufficiently large to be essentially constant during the reactions.

$$A_1 + O_3 \rightarrow a_1P_1 + \text{other products} \qquad (8)$$

$$A_2 + O_3 \rightarrow a_2P_2 + \text{other products} \qquad (9)$$

The ratio of the rate constants was obtained from Equation (10)

$$\frac{k_1}{k_2} = \frac{a_2}{a_1} \frac{(A_2)}{(A_1)} \frac{\Delta(P_1)}{\Delta(P_2)} \qquad (10)$$

(A_1) and (A_2) represented the concentrations of the two olefins; a_1 and a_2 were the stoichiometric coefficients; and $\Delta(P_1)$ and $\Delta(P_2)$ represented the changes in the concentrations of the two products being monitored. The stoichiometric coefficients were determined independently.

Vrbaski and Cvetanovic presented their results as k_1/k_{ref} in which ethylene was used as the reference substance, and k_{ref} was assigned a value of 1.0. The ratio k_1/k_{ref} was obtained from experimental data for k_1/k_2 and k_2/k_{ref}. In order to compare their results with the other data in Table II, the relative rate constants, k_1/k_{ref}, were multiplied by

1.4×10^3 liters/mole-second, which was the average of the absolute rate constants found in the literature for ethylene. The rate constants obtained by this competing method were generally lower than those reported based on other experimental methods.

Table III was taken directly from the work of Wei and Cvetanovic (1963). The values of k_{O_2} or k_{N_2} are the relative rate constants (with isobutene as the reference material and k_{ref} again assigned the value of 1.0) for the reaction between ozone and 2,3-dimethyl-2-butene with various olefins competing for the ozone. In several cases, the relative rate constants were determined by monitoring two different products. In all cases, the relative rate constants were obtained in the presence and absence of molecular oxygen. These data show that, depending upon the competing olefin used and the particular product monitored, the relative rate constant for the ozonation of 2,3-dimethyl-2-butene could differ by a factor of 2.1 or 1.5, depending on whether molecular oxygen was present or absent. Thus, the rate constants as determined by this method of competing reactions can be in error by a factor of about two, even before other experimental inaccuracies are considered.

The presence of molecular oxygen is also a significant factor with the ozone-olefin systems. Table IV, from Wei and Cvetanovic (1963), shows the relative rate constants determined in the presence and absence of oxygen. As in Table III the reaction of ozone with isobutene in the presence of

TABLE III

RELATIVE RATE OF REACTION OF OZONE WITH 2, 3 - DIMETHYL -2-

BUTENE AS DETERMINED COMPETITIVELY WITH DIFFERENT OLEFINS[a,b,c]

Competing Olefin	Product from Competing Olefin Monitored	k_{O_2}[d]	k_{N_2}[e]
1 - Butene	Propionaldehyde	4.0	5.4
1 - Pentene	Butyraldehyde	4.2	5.5
1 - Hexene	Valeraldehyde	4.6	6.6
3 - Methyl - 1 - Butene	Isobutyraldehyde	4.0	5.3
2 - Methyl - 1 - Butene	Methyl Ethyl Ketone	3.0	4.5
Cis - 2 - Butene	Acetaldehyde	5.6	5.5
Cis - 2 - Pentene	Acetaldehyde	5.5	5.9
Cis - 2 - Pentene	Propionaldehyde	5.6	5.8
2 - Hexene (Cis + Trans)	Acetaldehyde	5.2	5.8
2 - Hexene (Cis + Trans)	Butyraldehyde	6.0	6.2
4 - Methyl - 2 - Pentene	Acetaldehyde	5.1	5.2
4 - Methyl - 2 - Pentene	Isobutyraldehyde	6.3	6.4
3 - Methyl - 2 - Pentene	Acetaldehyde	4.0	4.7
3 - Methyl - 2 - Pentene	Methyl Ethyl Ketone	4.0	4.7

Notes: (a) Wei and Cvetanovic (1963).

(b) Assumed rate equation: $-\frac{dC_{HC}}{dt} = k\, C_{O_3}\, C_{HC}$

(c) Isobutene as reference material; for ozone-isobutene reaction $k_{O_2} = k_{N_2} = 1.0$ by definition

(d) Molecular oxygen present.

(e) Molecular oxygen absent.

molecular oxygen was taken as the reference for k_{O_2}; and similarly for k_{N_2}, the reaction of ozone with isobutene in the presence of nitrogen was taken as the reference. The value of k_{ref} was arbitrarily assigned a value of 1.0 for both k_{O_2} and k_{N_2} even though the actual absolute rates under these two reaction conditions may not have been the same. As a result, it is difficult to assess quantitatively the effect of molecular oxygen on the reaction rate constant because of the relative nature of these data. However, Wei and Cvetanovic did report that the presence of oxygen affected the stoichiometry of the ozone-olefin reactions. Their data showed that in the presence of oxygen the olefin to ozone consumption ratio ranged from about 1.4 to 2.0 depending upon the olefin while in the absence of oxygen this ratio was near unity. This was indicative of a secondary attack on the olefins in the presence of molecular oxygen. Cadle and Schadt (1952) and Bufalini and Altshuller (1965) also reported variable stoichiometry when the reaction was conducted with oxygen present.

The effect of temperature on the ozone-alkene hydrocarbon reactions has been studied only for five alkenes (Bufalini, 1965; Cadle, 1952). However, in all five cases the activation energy was significantly less than that for the ozone-alkane reactions.

TABLE IV

RELATIVE RATE CONSTANTS DETERMINED IN THE PRESENCE AND ABSENCE OF MOLECULAR OXYGEN[a,b,c]

Olefin	Competing Olefin	k_{O_2}[d]	k_{N_2}[e]
Ethylene	Isobutene	0.32	0.21
Propylene	Isobutene	1.30	0.95
1 - Butene	Isobutene	1.10	0.85
1 - Pentene	Isobutene	1.10	0.85
1 - Hexene	Isobutene	1.25	1.05
3 - Methyl - 1 - Butene	Isobutene	0.95	0.75
3 - Methyl - 1 - Pentene	Isobutene	0.90	0.75
4 - Methyl - 1 - Pentene	Isobutene	1.15	0.85
2 - Methyl - 1 - Butene	1 - Butene	1.30	1.25
2 - Methyl - 1 - Pentene	1 - Pentene	1.30	1.25
cis - 2 - Butene	Isobutene	3.4	2.0
trans - 2 - Butene	Isobutene	4.3	2.2
cis - 2 - Pentene	Isobutene	3.4	2.4
trans - 2 - Butene	Isobutene	4.2	2.8
2 - Hexene (cis + trans)	Isobutene	3.6	2.7
2 - Hexene (cis + trans)	2 - Methyl - 2 - Pentene	3.4	2.5
4 - Methyl - 2 - Pentene	Isobutene	3.5	2.4

TABLE IV (Continued)

RELATIVE RATE CONSTANTS DETERMINED IN THE PRESENCE AND ABSENCE OF MOLECULAR OXYGEN[a,b,c]

Olefin	Competing Olefin	k_{O_2}[d]	k_{N_2}[e]
2 - Methyl - 2 - Butene	1 - Butene	3.5	3.2
2 - Methyl - 2 - Pentene	3 - Methyl - 2 - Pentene	3.4	3.2
3 - Methyl - 2 - Pentene	Isobutene	3.5	3.3

Notes: (a) Wei and Cvetanovic (1963).

(b) Assumed rate equation: $-\frac{dC_{HC}}{dt} = k\, C_{O_3}\, C_{HC}$

(c) Isobutene as reference material; for ozone-isobutene reaction $k_{O_2} = k_{N_2} = 1.0$ by definition.

(d) Molecular oxygen present.

(e) Molecular oxygen absent.

Reactions of Other Hydrocarbons with Ozone

The kinetic constants for the ozone-alkyne hydrocarbon reactions are shown in Table V. These reactions were also reported to be first order with respect to both reactants. These rate constants were generally intermediate in magnitude between those of the alkanes and alkenes.

The initial concentration of the reactants was low, only a few ppm. No data at concentrations comparable to those employed in the alkane investigations were available. However, Dillemuth et al. (1962) noted that ozone-alkyne reactions proceeded with explosive violence at concentrations greater than a few ppm.

Table VI contains what is believed to be all of the existing reaction rate constant data for the aromatic hydrocarbon-ozone reactions. The much larger rate constant for styrene can be attributed to the relatively high reactivity of the olefinic double bond. These data also point to the greater resistance of the hybrid bond of the benzene ring to attack by ozone.

Of the oxygenated hydrocarbons present in contaminated air, the aldehydes appear to be most prevalent. Quantitative data on absolute rate constants were not found for the ozone-aldehyde reactions in the gas phase. However, Erickson et al. (1966) have presented some data on the reaction of ozone with benzaldehyde and substituted benzaldehydes at 0°C. In these studies the solvent had a substantial effect on the kinetics; but this factor is not relevant to gas phase reactions.

TABLE V

SUMMARY OF PAST WORK ON OZONE - ALKYNE REACTION KINETIC CONSTANTS

Compound	Oxygen Present	Initial Ozone Concentration (Moles/Liter)	Initial Hydrocarbon Concentration (Moles/Liter)	Pre-Exponential Factor[a] (Liters/Mole-Sec)	Activation Energy[a] (kcal/Mole)	k at 25°C[b] (Liters/Mole-Sec)	Reference
Acetylene	Yes[c]	10^{-5} (d)	10^{-5} (d)	1.2×10^{8}	4.8	36.	Cadle (1953) and Schubert (1956)
Propyne	Yes	2×10^{-10}	3×10^{-9}	-------	---	770.	Dillemuth(1962)
1 - Butyne	Yes	2×10^{-10}	3×10^{-9}	-------	---	1080.	Dillemuth(1962)

Notes: (a) Activation energy, E, defined by: $k = Ae^{-E/RT}$, where A is pre-exponential factor.

(b) Assumed rate equation: $-\frac{dCHC}{dt} = k\, C_{O_3}\, C_{HC}$

(c) Rate constant independent of pressure of carrier gas (oxygen and nitrogen).

(d) Assumed accuracy within order of magnitude.

TABLE VI

SUMMARY OF PAST WORK ON OZONE - AROMATIC REACTION KINETIC CONSTANTS

Compound	Oxygen Present	Initial Ozone Concentration[a] (Moles/Liter)	Initial Hydrocarbon Concentration[a] (Moles/Liter)	$k \times 10^{-3}$ at 25°C[b] (Liter/Mole-Sec)	Reference
1,3,5 - Trimethyl - Benzene	Yes	10^{-7}	10^{-7}	< 0.06[c]	Bufalini (1965)
Xylene	---	------	------	< 0.01	Hanst (1958)
Styrene	Yes	10^{-7}	10^{-7}	18.[c]	Bufalini (1965)

Notes: (a) Assumed accuracy within order of magnitude.

(b) Assumed rate equation: $-\frac{dC_{HC}}{dt} = k\, C_{O_3}\, C_{HC}$

(c) 30°C

PRESENT INVESTIGATION

Experimental

In the present studies a constant volume reactor was used to follow the reaction of ozone with ethylene by monitoring the change in total pressure. Both the ozone decomposition and ozone-ethylene reactions were investigated using this procedure.

A 1000 cc, 3-neck round bottom glass reactor was immersed in a constant temperature bath controlled to about 25°C. The reactor was connected to a 100 inch sulfuric acid manometer.

CP grade ethylene (Matheson Co., 99.0 mole% ethylene, 0.15% methane, and less than 50 ppm of ethane, propane, propylene, and acetylene) and ozone dissolved in Freon-13 ($CClF_3$) (Matheson Co.) were fed from cylinders. In some runs the system was swept with dry nitrogen and in others with dry oxygen prior to feeding the reactants. The ozone cylinder was discharged in an inverted position, and the ozone Freon-13 mixture vaporized prior to entering the reactor. Bottled ozone dissolved in Freon-13 was a convenient source of ozone both for the higher concentrations desired in this initial work and also for obtaining ozone with a minimum of oxygen present.

Ozone concentrations were determined prior to a run by passing a known volume of gas through 2% potassium iodide solution, and titrating the released iodine with 0.1 N sodium thiosulfate with starch indicator. The initial cylinder ozone concentration was about 5 mole% but after forty-five days had decreased to 0.5 mole%. This decomposition occurred despite storage in an insulated container at dry ice temperature.

The initial ozone partial pressure in the reactor was always less than 9 mm Hg, and the pressure changes that occurred during reaction were several mm Hg. The reactor temperature was continuously monitored, and the data were corrected to 25°C to compensate for temperature fluctuations due to the heat of reaction and to cycling of the bath controller.

Discussion of Results

The ozone decomposition rate was first order. The data are plotted in Figure 1. This rate is much higher than that predicted by Benson and Axworthy (1957) or Zaslowsky et al. (1960). This suggests that either reactions involving Freon-13 or catalytic effects were important in the ozone decomposition process.

For the ozone-ethylene runs the initial reactant ratio (defined as the initial partial pressure of ethylene divided by the initial partial pressure of ozone, or

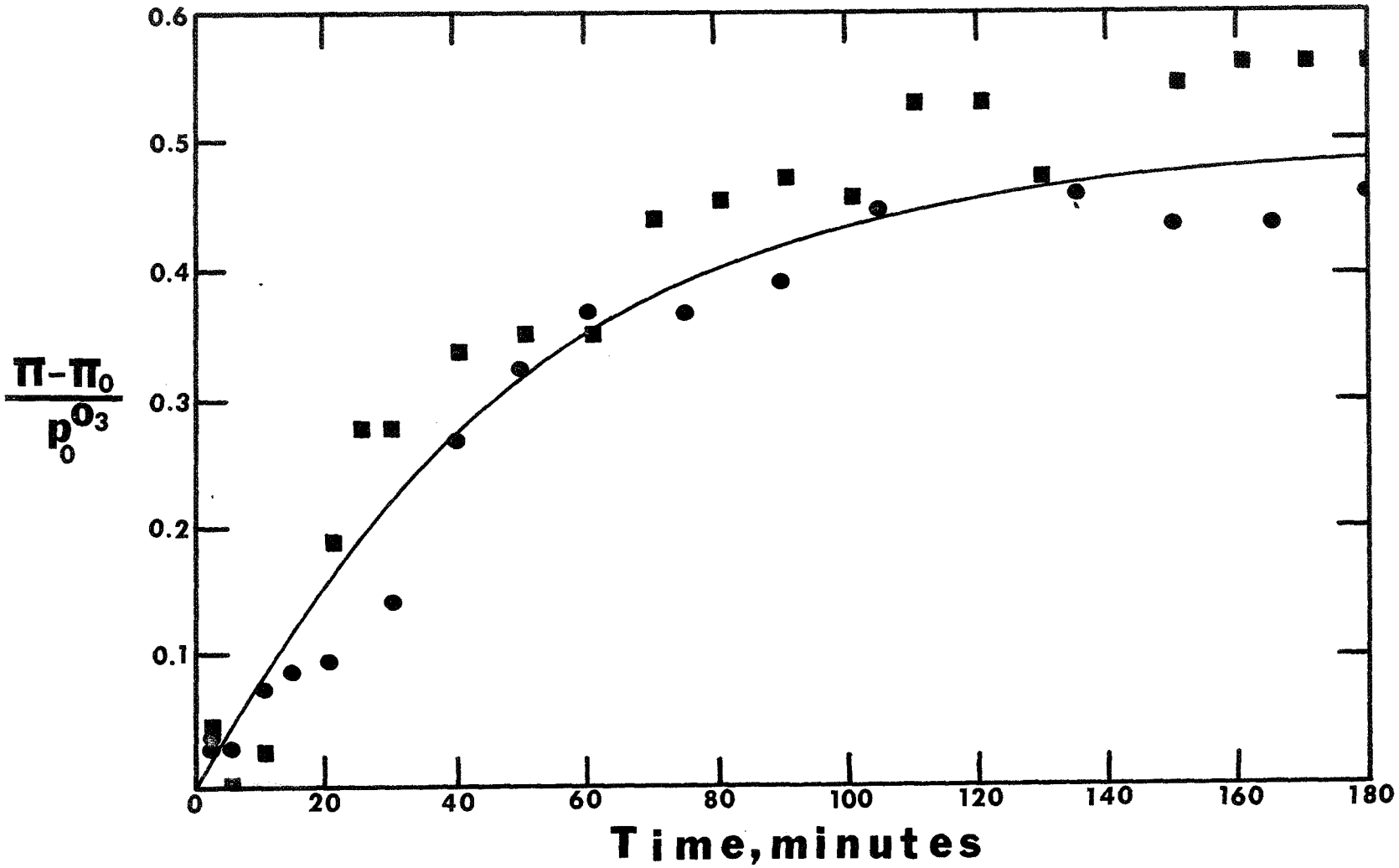

Figure 1

Dimensionless pressure increase as a function of time for ozone decomposition. Circular and square data points are from different runs.

$P_o^{C_2H_4}/P_o^{O_3}$) ranged from 0.80 to 57. Figure 2 shows the change in reactor pressure divided by the starting ozone partial pressure, $(\pi - \pi_o)/P_o^{O_3}$, as a function of initial reactant ratio for eight different runs and for reaction time periods of 15, 30, and 60 minutes. π represents the total pressure in the reactor at any time, and π_o represents the initial total pressure. The reactor was flushed with nitrogen prior to feeding the reactants for these runs.

This dimensionless pressure parameter, $(\pi - \pi_o)/P_o^{O_3}$, is an indication of the stoichiometry of the reaction. Consider the generalized stoichiometry for the ozone oxidation of ethylene, where a, b, and c represent the stoichiometric coefficients.

$$aC_2H_4 + bO_3 \rightarrow c \text{ Products} \qquad (1)$$

Assuming that the ideal gas law holds for the reaction mixture, the pressure change during the gas phase reaction due to a change in the number of moles is

$$\pi - \pi_o = \frac{c - (a + b)}{b} (P_o^{O_3} - P^{O_3}) \qquad (2)$$

Multiplying Equation (2) by $P_o^{C_2H_4}/P_o^{O_3}$ gives Equation (3).

$$\frac{\pi - \pi_o}{P_o^{O_3}} = \frac{c - (a + b)}{b} \left(\frac{P_o^{O_3} - P^{O_3}}{P_o^{C_2H_4}}\right) \left(\frac{P_o^{C_2H_4}}{P_o^{O_3}}\right) \qquad (3)$$

In theory if only one reaction is involved, the ratio

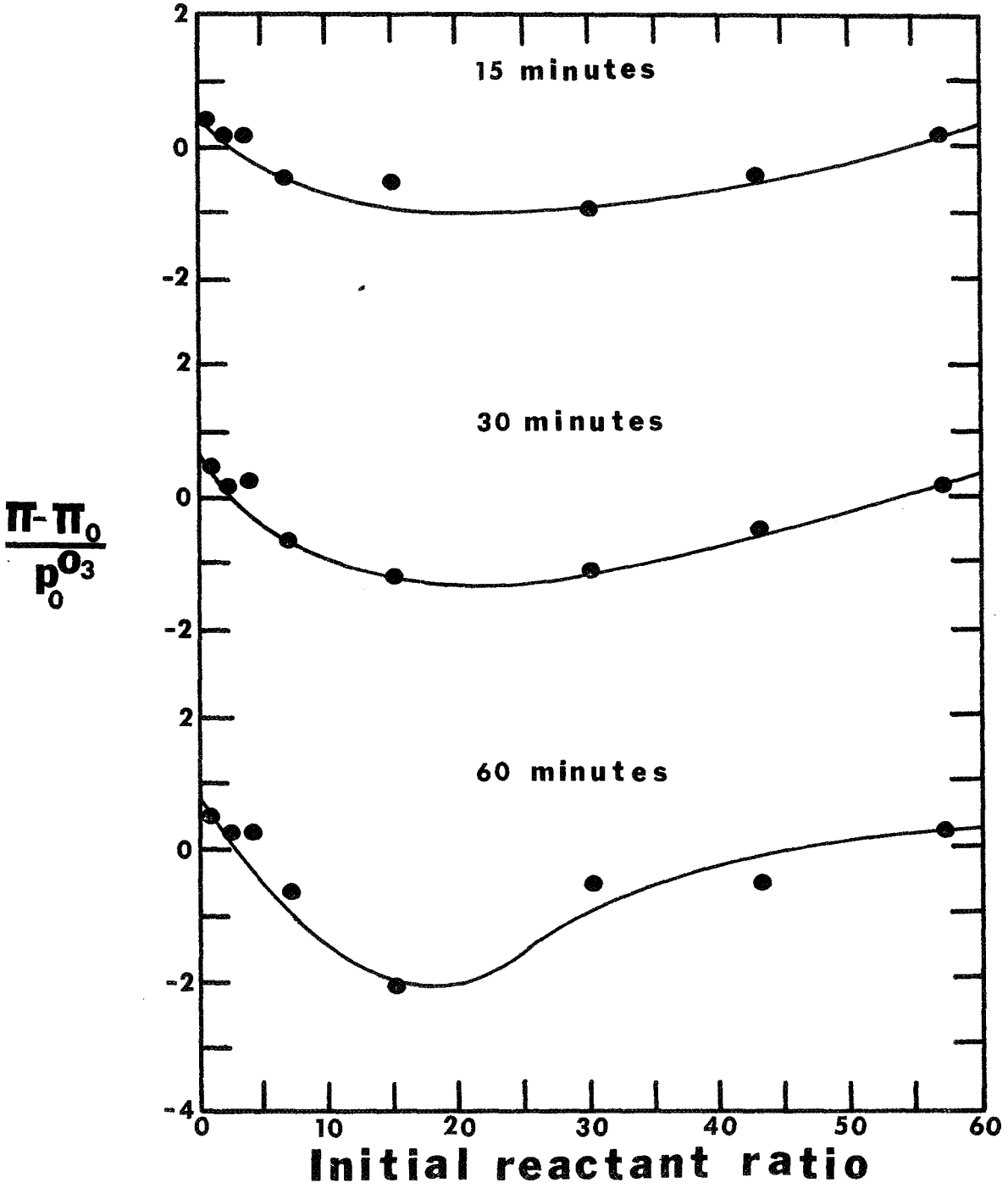

Figure 2

Dimensionless pressure increase as a function of initial reactant ratio for system flushed with nitrogen.

$(\pi - \pi_o)/P_{O_3}^o$ could not change sign. It follows from Equation (3) that the sign is determined only by the magnitudes of a, b, and c and is independent of the initial reactant ratio. Furthermore, if the reaction were permitted to go to completion in the presence of excess ethylene, $(\pi - \pi_o)/P_{O_3}^o$ should be constant at $(c - (a + b))/b$.

In Figure 2, the sign of the dimensionless pressure parameter changed at initial reactant ratios of about three and fifty-five. Furthermore, $(\pi - \pi_o)/P_{O_3}^o$ did not become constant as the reaction proceeded even with a large excess of ethylene. Both of these factors show that more than one reaction was involved.

Obviously, one of the competing reactions was the decomposition of ozone, which in theory would be most important at low initial reactant ratios. However, the data obtained at low initial reactant ratios showed that $(\pi - \pi_o)/P_{O_3}^o$ would change from positive to negative even when adjusted for background ozone decomposition. Furthermore, at the higher initial reactant ratios, where the ozone decomposition should be relatively insignificant, $(\pi - \pi_o)/P_{O_3}^o$ again changed sign. Both factors indicate that, in addition to the decomposition of ozone, at least two competing reactions must have been present. Gas chromatographic analyses of several of the experimental runs also supported this conclusion.

In Figure 3 data points from two experimental runs in which oxygen was used to flush the system are compared with the curves from Figure 2 (nitrogen flush). It indicates that the level of oxygen concentration apparently can affect

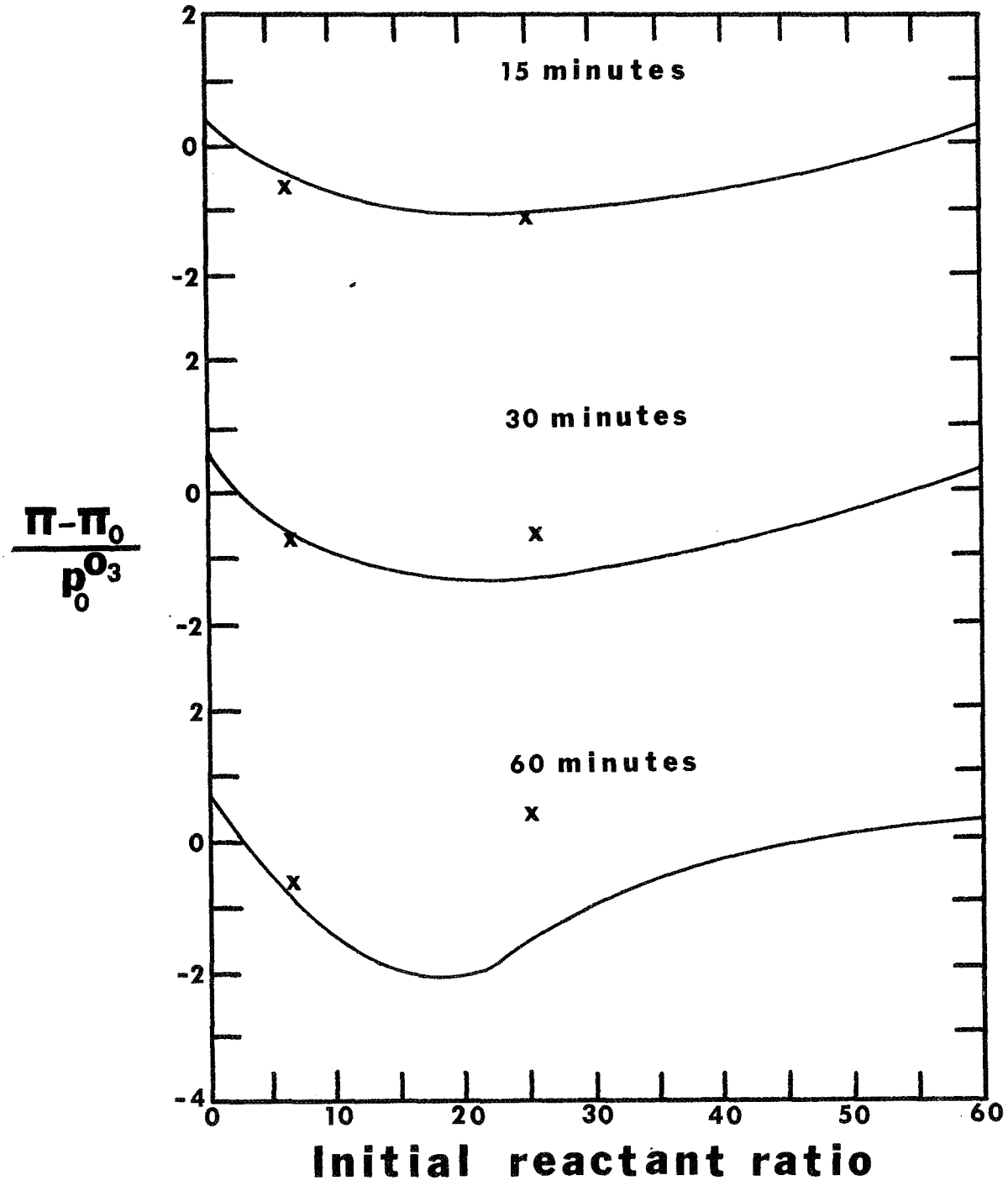

Figure 3

_____ = System flushed with nitrogen

x = System flushed with oxygen

the mechanism of the ozone-olefin reaction, especially after longer reaction times. This fact agrees with the previous findings of Wei and Cvetanovic (1963).

The reactant ratio for the ozone-ethylene reaction in urban atmospheres is about one. Total atmospheric hydrocarbon to oxidant ratios are on the order of 60 to 300 (Larsen, 1967 and Stern, 1968, p. 33); the olefin to oxidant ratio would, of course, be lower. Altshuller's (1966) tabulation indicates that the ethylene concentration is in the same order of magnitude as the ozone concentration in polluted atmospheres.

Conclusions

In the system used, the rate of ozone decomposition was much higher than that predicted by published data. Apparently, catalytic effects or possibly reactions involving the Freon-13 were important. The decomposition of ozone is known to be catalyzed by many substances. In addition, these experiments showed that the ozone-ethylene reaction kinetics were significantly affected by the initial reactant ratio and that competing reactions were present. Literature values for kinetic rate constants for some other olefins show considerable variation. The presence of competing reactions may in part be responsible for these discrepancies. The ozone-olefin reactions may not be strictly second order as usually has been assumed in calculating the rate constants. Finally, our data agreed with the findings of Wei and Cvetanovic (1963) that the presence of molecular oxygen affects the ozone-olefin reactions.

SUGGESTIONS FOR FUTURE WORK

Assuming that the reaction sequence (Reactions 1-4) cited earlier for smog formation is correct, it would be exceedingly helpful to know quantitatively the extent of participation of Reaction 3 (ozone) and Reaction 4 (atomic oxygen) for a variety of hydrocarbons. Such quantitative rate data would enable one to predict the extent of smog formation for a variety of hydrocarbons and under actual urban atmospheric conditions.

Since the low molecular weight alkanes, alkenes and aldehydes have been found most prevalent in smog forming areas, their reactions with ozone and with atomic oxygen need the greatest attention. Unless the atmospheric concentrations of the slower reacting alkanes are significantly higher than those of the other two groups, the alkene and aldehyde reactions should receive the most attention. Specific recommendations follow.

1. More reliable rate constants are needed for the reaction of ozone with C_3 and C_4 alkenes and with low molecular weight aldehydes.

2. More reliable activation energy and pre-exponential factor data are needed for C_2 thru C_4 alkenes and low molecular weight aldehydes. These are needed for the quantitative prediction of temperature variations on smog formation.

3. Experimentally, it is extremely difficult to carry out ozone reactions in the complete absence of molecular or atomic oxygen. However, it remains to be established whether the presence of atomic oxygen affects the rate of Reaction 3 or the presence of ozone affects the rate of Reaction 4. In other words is there a synergistic effect between these two reactions in the absence of ultra-violet radiation?

4. Similarly, does the initial ratio of hydrocarbon to ozone or hydrocarbon to atomic oxygen affect either the rate of reaction, the apparent reaction mechanism, or the rate of decomposition of ozone? The results contained in this report suggest significant effects, at least in the presence of chlorotrifluoromethane.

5. Are the rates of Reaction 3 or Reaction 4 affected through heterogeneous catalysis by solid particulate matter found in urban atmospheres?

6. Each of the above recommendations should be examined further to see if the presence of ultra-violet radiation affects the rate and especially if a synergistic effect is noted between the ozone and atomic oxygen reactions.

7. Similarly, the effect of molecular oxygen on the rate and mechanism of the ozone-alkene reactions remains to be determined. Qualitative data indicate a significant effect,

but quantitative data are still not clear. The experimental problems are formidable; the use of a gas chromatographic reactor with the ozone-oxygen mixture the mobile phase and the hydrocarbon the stationary phase should provide definitive results.

8. And finally, it must be verified experimentally whether or not the rate constant is changed as the concentration of ozone and hydrocarbon are reduced to the levels found in urban atmospheres, that is to concentrations of 1 ppm or less. Much of the present literature data are at higher concentrations, and the question has been raised as to whether these data are applicable at the very low concentrations found in practice. This question is especially pertinent if surface catalysis with airborne particulate matter is a significant effect in smog formation. Experimentally it is not easy to simultaneously analyze for ozone and hydrocarbons, especially at initial concentrations of 1 ppm or lower. Two procedures are suggested. A gas chromatographic reactor using either conventional detectors or a mass spectrometer detector should enable experiments to be conducted at initial concentrations of a few ppm. Secondly, a flow reactor with view ports positioned along the reactor length for analysis using infra-red spectrophotometry should also be applicable for work in the few ppm range. On the latter method the IR beam would need to be reflected several times through the reacting mixture to provide sufficient absorption

at these low concentrations to follow changes in the ozone and hydrocarbon concentrations. Although ozone has its strongest absorption band in the UV, the presence of UV radiation might modify the results (Recommendation 6).

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